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SERS Active Surface in Two Steps, Patterning and Metallization**

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Robust and reproducible metallized nano/microstructured surfaces of polymeric surfaces have been successfully prepared by direct laser interference patterning (DLIP) of commercial polymeric films followed by sputtering of metallic thin films. The SERS spectra for 2-thioaniline adsorbed on a structured polycarbonate surfaces covered with a gold or platinum film showed a ca. three order of magnitude enhancement over a flat surface with the same metal film. The method here reported is suitable for mass production of substrates for SERS since large areas (several cm²) can be structured in ca. 1–5 s.

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Surface-enhanced Raman spectroscopy (SERS) is currently the only tool capable of combining chemical information with single molecule sensitivity making it one of the most powerful analytical techniques. SERS is characterized by a dramatic enhancement of the Raman signal when molecules are adsorbed onto micro/nano-sized metal surfaces. Since its discovery 25 years ago,^[1] many attempts have been done in producing SERS-active substrates by controlling the size, shape, and spacing of the metallic surface. However, the production of a uniform and reproducible substrate is today the major issue of researchers interested in developing active-SERS surfaces.^[2–5] In the present communication a fast and simple method, based on the formation of SERS active nano/microstructured surfaces by laser ablation, is described.

Lithographic techniques are usually employed to produce these long-range order structured surfaces. However, it consists of several steps such as exposure and etching and in many cases a mask must be fabricated. Moreover, most lithographic techniques are not capable of producing feature sizes small enough to be truly SERS-active. Because of its intrinsic resolution, electron beam lithography is currently the best procedure for nano-fabrication since it can build structures on a smaller scale and can be used to directly create nanometer features.^[6] However, electron beam is not yet appropriate for mass production since it is a time consuming process and expensive.

Other approaches involve template directed synthesis techniques.^[7–9] However, the mandatory use of conducting underlying surfaces and the need of many processing steps to produce the arrays may limit the extent of this method to mass production.

Recently, it has been reported a method for preparing SERS substrates that involves the metallization of nanostructured polymers obtained by an oblique angle polymerization method.^[10]

Here, we describe the fabrication and application of a SERS-active substrate consisting of the metallization of polymeric surfaces structured by using direct laser interference patterning (DLIP).^[11] The method has important advantages such as: (i) uniformity: periodic structures with a very well order in the range of sub-micrometer to several micrometers can be fabricated in one step; (ii) speed: several square centimeters can be patterned in a few seconds (up to $\approx 50 \text{ cm}^2 \text{ s}^{-1}$); (iii) simplicity: the substrates can be patterned directly in air without the use of special installations, such as ultra clean rooms or vacuum chamber; (iv) low fabrication costs: the substrates manufactured in a quick and simple manner make commercialization of these feasible.

In DLIP no masks are needed, and the structures are produced without any secondary step (e.g., etching) by the direct interaction of the laser light with the material (e.g., by photothermal, photochemical, or photophysical ablation).^[12] Additionally, the control of sample vibrations is much less stringent since only one pulse of some nanoseconds is necessary unlike typical photolithographic process (up to several minutes). Due to the solid nature of the material, it is also possible to pattern samples with different shapes (even non-planar) at any position. The shape and dimension of the interference patterns can be adjusted by controlling the number of laser beams as well as their geometrical configuration.

1. Results and Discussion

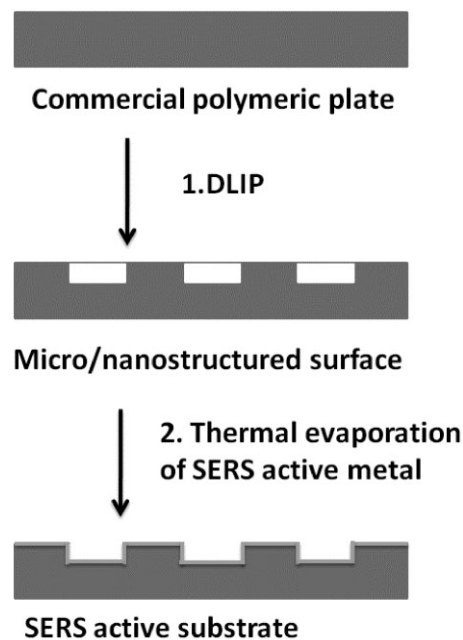
In Scheme 1, it is depicted our approach for SERS substrate preparation.^[13] First, a polymer plate is irradiated using a short pulse (10 ns) of high energy laser ($>300 \text{ mJ}$) at a suitable wavelength (e.g., 266 nm). The fundamental laser beam is split into two or three sub-beams to produce periodic patterns on the polymer (Step 1). After that, a SERS-active metallic layer (Au, Ag, or Pt) is deposited onto the micro/nanostructured polymer by thermal evaporation or sputtering (Step 2). By controlling the incident angles of the individual laser beams, it is possible to produce different geometries and periods to obtain the largest enhancement of the Raman signal.

In the case of two-beam interference experiments, the period (P) of the periodic line-like pattern is described by the Equation (1).^[11,12]

$$P = \frac{\lambda}{2 \sin \alpha} \quad (1)$$

where (α) is the angle between the laser beams, and (λ) is the laser light wavelength. As it can be observed, smaller wavelengths and larger angles permit to obtain smaller periodic distances.^[12]

To fabricate grid-like structures, the polymeric substrate can be first irradiated with the two-beam configuration using one laser pulse (10 ns) obtaining a line-like array, then the substrate is rotated 90° and a second laser pulse is irradiated on the surface (Figure 1).



Scheme 1. Fabrication Procedure of Patterned polymer/metal SERS-active surfaces. (1) DLIP of PC; (2) SERS-active metal deposition.

In Figure 1a, the two laser pulses had the same energy density (193 mJ cm^{-2}), while in Figure 1b the second pulse had higher intensity (250 mJ cm^{-2}) than the first one (193 mJ cm^{-2}). In the last case, the line-like structure induced by the second pulse predominates. In both cases, well-defined arrays of grid-structures with a long-range order (mm–cm) could be fabricated. Moreover, the widths of the lines as well as their separation (periodic distance $\approx 5.6 \mu\text{m}$) are very regular throughout the analyzed area. In addition, it can be noticed that the structure depth is dependent on the laser intensity (Figure 1).

Similarly, three-beam interference patterns produce different 2D arrays depending on the magnitude of the partial intensity of each beam as well as their geometrical configuration.

Figure 2 shows two different structures of polycarbonate obtained using a three-beam laser configuration. In the case of Figure 2a, the energy of each individual beam was identical giving a crater-like pattern with a hexagonal intensity distribution. In the second case (Figure 2b), the same procedure was employed, increasing the path of one incident sub-beam. Therefore a similar distribution is obtained in which the features are connected by one end along the y -axis. This axis corresponds to the sub-beam with longer path, that is, less energy and subsequently its contribution to the interference pattern is smaller.

For SERS it is known that stronger enhancements come from sharp features and areas of large curvature. The main feature sizes showed here (in the order of micrometer) could not be enough to produce SERS effect since they are larger than the wavelengths employed in Raman experiments, decreasing the sensibility. However, the feature size can be

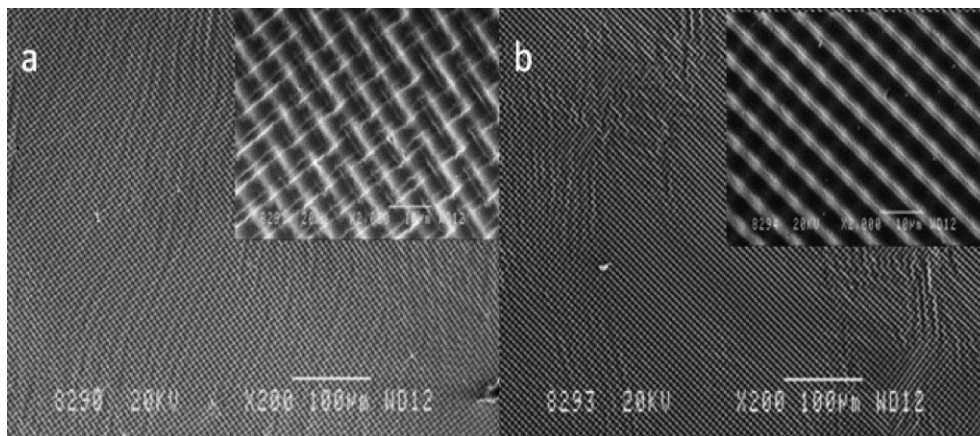


Fig. 1. SEM images of grid-like microstructures on PC surfaces obtained using two laser pulses in orthogonal direction using: (a) two laser pulses with same laser fluence (193 mJ cm^{-2}); and (b) first pulse with a laser fluence of 193 mJ cm^{-2} and second pulse with 250 mJ cm^{-2} .

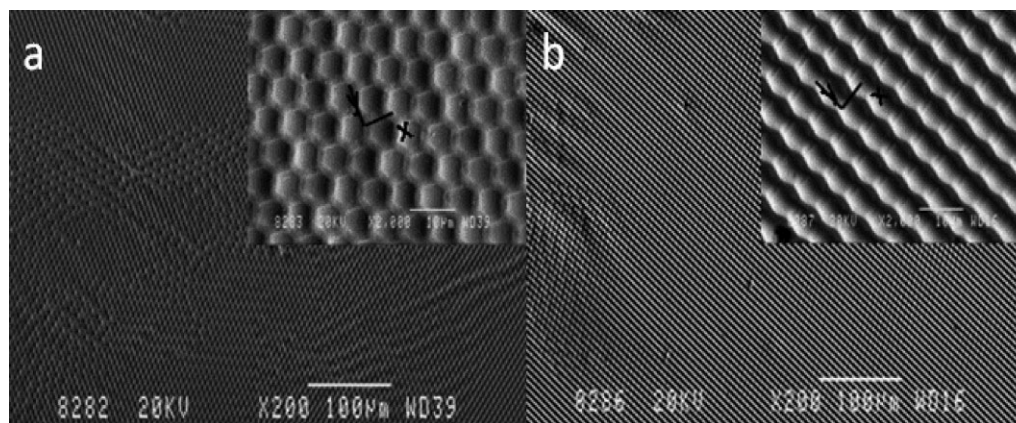


Fig. 2. SEM images of hexagonal grid-like microstructures on PC surfaces using a laser fluence of 300 mJ cm^{-2} . In (a), the main laser beam was split into a three equally energetic sub-beams, while in (b) the path of one incident sub-beam was increased.

tuned by using a more energetic laser beam to make it narrower.

The suitability for SERS of the DLIP-structured polycarbonate covered with 500 nm of Au and Pt was tested using 2-thioaniline as target molecule (Figure 3).

The Raman spectra of 2-thioaniline adsorbed onto structured and smooth polycarbonate/Au surfaces are shown in Figure 3a. The spectra agree well with those in the literature for 2-thioaniline on gold substrates.^[16] The SERS intensity obtained in the structured zones was significantly greater, around three orders of magnitude, than that for the smooth surface. Also, the effect occurred in both grid and crater-like structures, being more notorious in the former. These samples are not only different in shape but also in the period. Therefore, both parameters can be responsible for the different enhancement on the Raman signal. To tune the surface plasmon resonances to maximize signal strength and ensure reproducibility may require control of the size, shape, spacing, and material of the structure.^[2,14,15] DLIP has the advantage that these parameters can be easily controlled by tailoring the

number of sub-beams on which the main beam is split (shape), tuning the laser energy (size), and/or the sub-beams angle (period).

In addition, the grid-like array created using 193 and 250 mJ cm^{-2} in the orthogonal plane (Figure 1b) did not enhance significantly the Raman signal with respect to the unstructured surface (not shown). It is likely that the actual dimensions after the metallization remain above the wavelength of the laser employed in the Raman experiment ($\lambda = 632 \text{ nm}$), making the enhancement smaller. In fact, it seems that the voids between lines are bigger and the surface resembles an array of lines. It is important to remark that Raman spectra were collected in different zones and the variation of the SERS signal across the structured zones was around 5% that confirms the homogeneity of the surfaces obtained by the described procedure.

Although Pt has been commonly considered as non-SERS-active substrate, recently SERS effect has been reported using platinum nanostructures.^[9,15–17] Figure 3b shows the Raman spectra of 2-thioaniline adsorbed onto structured and

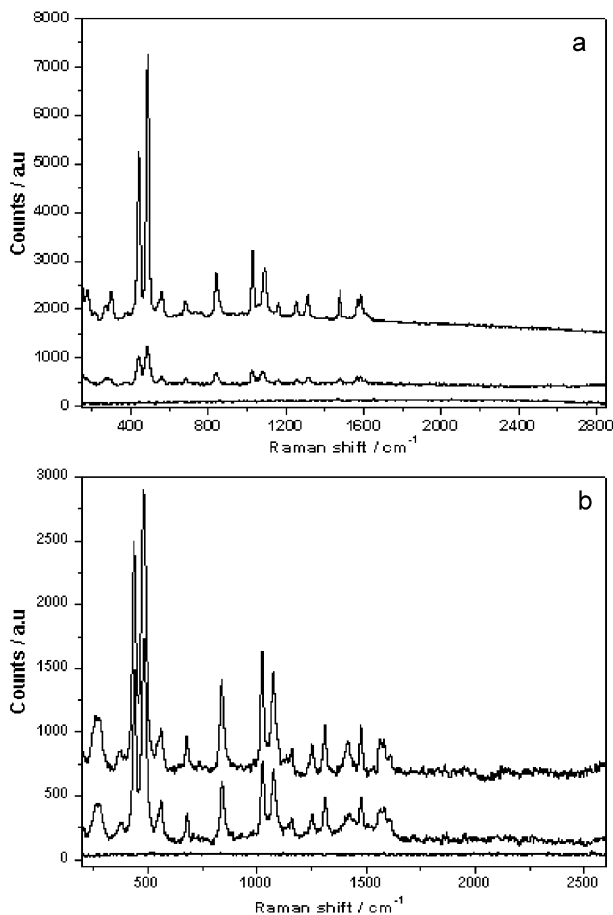


Fig. 3. Raman spectra of 2-thioaniline absorbed onto DLIP-microstructured PC surfaces covered with 500 nm active SERS metals: (a) gold, (b) platinum. Top: grid-like structures. Middle: hexagonal structures. Down: unstructured surfaces. The sampling time to acquire the Raman spectra was 5 s, except for the grid-like array in (a) with 2 s.

smooth polycarbonate/Pt surfaces. The SERS intensity obtained in the structured zones was also significantly enhanced, respect to the smooth surface. The enhancement occurred in both grating-like and hole-like structured surfaces. The spectra agree well with those in polycarbonate/Au surfaces (Figure 3a) in terms of both, band positions and relative intensities. It seems that the 2-thioaniline adsorbs onto both metal through S–M linkage since no band for S–H stretching (near 2500 cm^{-1}) is observed. Comparing the intensity of the principal bands of 2-thioaniline it can be perceived that it is 40–50% lower for Pt-covered polycarbonate than for Au-covered surfaces. This is a logical behavior because of the enhancement scales as the fourth power of the local metallic nanostructure field,^[15] which depend on the employed material. On the other hand, Pt has interesting electrocatalytic properties which make it more interesting as SERS substrate in electrochemical applications.^[18]

While the data shown uses structured polycarbonate as substrate, the approach is general and can be extended to other polymers. In fact, well-ordered arrays have also been prepared using polymers with high absorption coefficient in the UV-visible region, such as polyimide

(PI),^[11] polyetherimide (PEI),^[11,12] poly(ether ether ketone) (PEEK),^[11] polyaniline (PANI),^[12] polystyrene, and its copolymer with acrylic monomer.

In summary, we have described a simple method to prepare SERS active substrates by which homogenous structured surfaces in the order of several cm^2 can be prepared in a few seconds. Our method dispense with the use of nanoparticles, avoiding problems of variations in particle or colloid size. Therefore, this approach ensures reproducibility and stability, which are essential for SERS-active substrates. So far, to make SERS-optimized substrates, nanostructured surfaces have been made by multi-step expensive lithographic techniques. Here a quick, inexpensive, and clean approach ideal for mass production of SERS-active surfaces has been described.

Besides its simplicity, the method allows the pattern shape to be tailored easily by simply changing the geometry of the optical set-up. In that way, both optimization of the SERS effect and better understanding on the effect of surface geometry on the nature of the plasmons can be obtained.

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